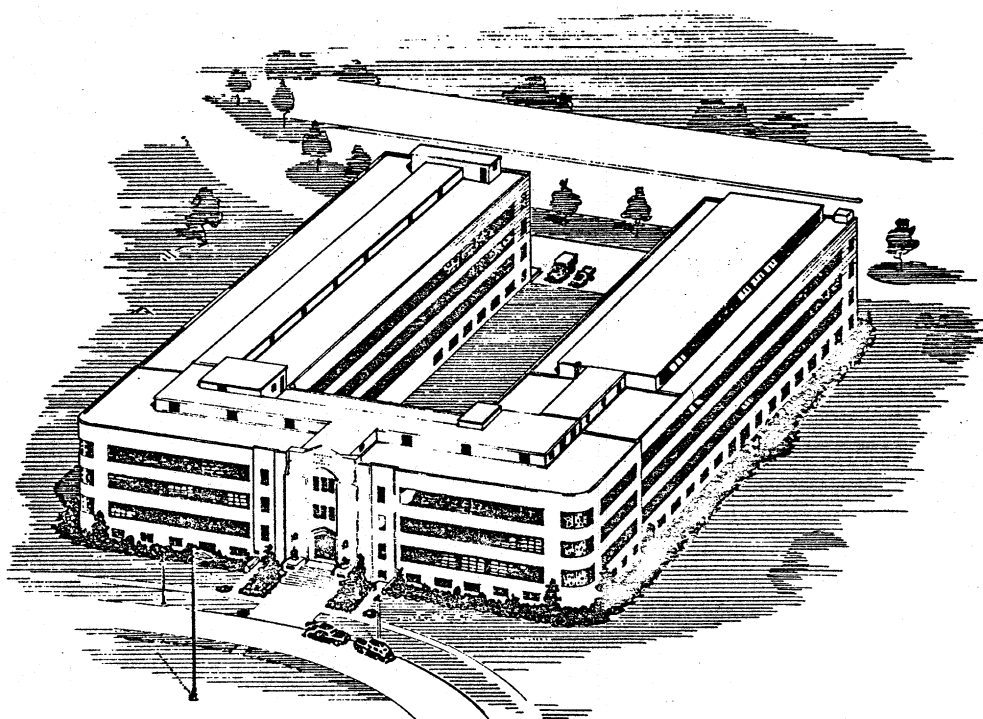


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The extensive patent literature on polyhydric alcohol esters reflects the unusual interest of industry in these materials. In 1943, Goldsmith (1) reviewed the methods of preparation and the industrial application of the higher fatty acid esters of polyhydric alcohols. Considerable data have been accumulated on the physical and chemical properties of esters of ethylene glycol, glycerol, mannitol and glucose, but little information can be found on similar derivatives of sucrose. In this paper the properties of completely or almost completely substituted saturated esters of sucrose are described. The properties of six unsaturated esters of sucrose were reported recently (2). Partially esterified sucrose derivatives will be described later.

The lower saturated fatty acid esters of sucrose can be prepared in good yield by acylation with the anhydride of the acid in the presence of pyridine or sodium acetate. Octaacetyl (3), octapropionyl (4), and octabutyrylsucrose (4) can be prepared readily in the laboratory in this manner. Of this group, octaacetylsucrose is the only fatty acid ester of sucrose commercially available at present. Pilot plant production of the acetate from sucrose, acetic anhydride, and fused sodium acetate has also been reported (5). Octapalmitoyl (6) and octastearoylsucrose (6) have been prepared by treating sucrose with the corresponding acid chloride in a mixture of pyridine and chloroform. The chloroform is added to dissolve the acid chloride-pyridine complex (7). In our work the propionyl and butyryl derivatives were also prepared with the corresponding anhydrides (Table I); the rest of the derivatives listed were prepared from the appropriate acid chlorides. Direct esterification of sucrose (8) with fatty acids, without catalyst, has been described, but yields were poor even after long periods of heating at high temperature. Boulez (9), however, claimed that octaacetylsucrose can be prepared from sucrose and acetic acid in good yield; but details were not reported.

The acetyl, propionyl, palmitoyl, and stearoyl derivatives are reported in the literature to be solids of low-melting point. We found that the myristoyl, palmitoyl, and stearoyl derivatives can easily be obtained in a solid form. The properties of the acetyl derivative, which has received particular attention, are already well known. Though the propionyl derivative showed no tendency to crystallize, it has been reported that seed crystals give good yields of solid material (4a). The butyryl, caproyl, caprylyl, and capryl derivatives were sirups; the lauroyl ester was a colorless, sticky semi-solid. Because the relatively high molecular weights of these products paralleled high boiling points, the liquids were not distilled. Impurities were removed by washing chloroform solutions of the derivatives with dilute acid, sodium bicarbonate, and finally, with water. The fairly good agreement of the saponification equivalents with the theoretical values given in Table I indicates that the products were substantially pure.

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Table I. Properties of Saturated Esters of Sucrose

Octa substituted derivatives of sucrose	Formula	M.P., °C.	Yield	Saponification equivalent	Found	OH %	Unreacted OH groups	$[\alpha]_D^{25}$	n_D^{25}	Physical appearance	Mol. Wt. calcd. for octa deriv.
ACETYL	C ₂₈ H ₃₈ O ₁₉	^b	82.3	98.8	96.1	0.0	0.0	+51.8	1.4588	Colorless sirup	790.6
PROPIONYL	C ₃₆ H ₅₄ O ₁₉	^c	86.5	112.8	110.4	0.0	0.0	+46.0	1.4550	Lt. yellow sirup	902.6
BUTYRYL ^d	C ₄₄ H ₇₀ O ₁₉		81.8	140.8	144.0	0.75	0.2	+33.4	1.4582	Brown sirup	1126.6
CAPROYL ^e	C ₇₆ H ₁₃₄ O ₁₉		86.4	168.8	169.2	0.0	0.0	+26.7	1.4615	Brown sirup	1350.6
CAPRYL ^e	C ₉₂ H ₁₆₆ O ₁₉		78.0	196.8	200.9	0.21	0.2	+19.7	1.4677	Brown sirup	1574.6
LAUROYL ^e	C ₁₀₈ H ₁₉₈ O ₁₉		70.0	224.8	225.2	0.0	0.0	+20.7	1.4683	Colorless semi-solid	1798.8
MYRISTOYL ^e	C ₁₂₄ H ₂₃₀ O ₁₉	41.42	86.8	252.8	256	0.26	0.3	+18.0	..	Off-white amorphous powder	2022.8
PALMITOYL ^{f,g}	C ₁₂₄ H ₂₃₂ O ₁₈	52.53	77.0	286.7	289	0.8	0.9	+17.4		Ditto	2007.4 (hepta)
STEAROYL ^h	C ₁₅₆ H ₂₉₄ O ₁₉	60.61	81.0	309	305	0.4	0.5	+16.9		White amorphous powder	2470.8

- a. All rotations cited are specific rotations of the D line of sodium at 25°.
- b. Reported by Hudson and Johnson (3c), M.P., 89°; Brigl and Scheyer (3d), M.P., 75°; Frèrejacque (3e), M.P. 87°; Sander (3f), M.P., 83°; Linsted et al., (3g), M.P., 89°. It has been shown (3g) that octaacetylsucrose is polymorphous and the form melting at 89° is the most stable modification.
- c. Reported by Hurd and Gordon (4a), M.P., 45-46°; Cox, Ferguson and Dodds (5), M.P., 45.4-45.5°.
- d. Reported by Wolff (4b) for Sirup $[\alpha]_D^{25} +46.5$ (CHCl₃); Cox, Ferguson and Dodds (5).
- e. These compounds are believed to be previously unreported in the literature.
- f. Analysis for sapon. equiv. and unreacted OH groups suggest a hepta derivative.
- g. Reported by Hess and Messmer (6), M.P., 54-55° (for octa derivative).
- h. Reported by Hess and Messmer (6), M.P., 57°.

With increasing molecular weights of the esters, the specific rotation decreases and the index of refraction increases. The rotation of the lauroyl derivative and refractive index of the propionyl derivative, however, are exceptions. As changes in rotation are fairly small from the capryl through the stearoyl derivatives, impurities such as free acid admixed with the capryl or lauroyl ester would account for the anomalous rotation of the laurate. An explanation for the high refractive index of propionylsucrose may be found in the fact that propionic acid is the only fatty acid in Table I with an odd number of carbon atoms. The alternating pattern of the even and odd members of the fatty acid series, characteristic of melting points particularly, is well known.

At room temperature, the esters are readily soluble in non-polar solvents such as ether, chloroform and benzene. All except the palmitoyl and stearoyl derivatives are soluble in acetone. The esters below lauroyl are soluble in ethyl alcohol; the lauroyl and higher esters are difficultly soluble. In methyl alcohol the acetyl through the caproyl derivatives are soluble; the higher esters are practically insoluble.

No serious attempt to crystallize the sirupy esters was undertaken. For many industrial uses, the liquids may be preferred. All the esters were tested as plasticizers for Vinylite VYDR (polyvinyl chloride-acetate). Octapropionylsucrose alone was compatible with the VYDR, but this derivative proved to be relatively inefficient when compared with a dioctyl phthalate control.

EXPERIMENTAL

Starting Materials.--Propionic and butyric anhydrides, obtained from commercial sources, were used without further purification. The acid chlorides were prepared from the corresponding acid and thionyl chloride (10). The crude acid chlorides were fractionated, and the fractions identical in boiling point with those reported in the literature were used.

Esterification Methods:

A. Acylation with Anhydrides.--Finely powdered sucrose (34.2 g., 0.1 mole) and pyridine (126 g., 1.6 mole) were placed in a 500-cc. three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel. The anhydride (1.2 moles) was added slowly at room temperature, with rapid stirring. After the addition of the anhydride, the mixture was heated at 100° C. for one and one-half hours. The clear solution was allowed to stand at room temperature for twenty-four hours and then concentrated *in vacuo* with a bath temperature of 70-90° C. The residue was dissolved in chloroform, and the chloroform solution was washed with 10 percent sulfuric acid, saturated sodium bicarbonate solution, and finally with water. The chloroform layer was dried over anhydrous sodium sulfate, then concentrated *in vacuo*.

B. Acylation with Acid Chloride.--Sucrose (34.2 g., 0.1 mole) was suspended in a mixture of pyridine (126 g., 1.6 mole) and chloroform (165 cc.). The appropriate acid chloride (0.88 mole) in 115 cc. of chloroform was added

slowly at 0° C., with rapid stirring. After the reagents were mixed, the flask was allowed to reach room temperature, then heated at 70-90° for two hours, and allowed to stand overnight. The lower layer was discarded. Ether was added to the upper layer until no more precipitate separated. The ethereal solution was filtered, then concentrated *in vacuo*. In preparing the caprylyl and higher derivatives, the residue was washed with methyl alcohol to remove pyridine and excess acid chloride. In all cases the product was then dissolved in chloroform and worked up as described in A.

Analyses.—Acyl analyses were carried out by saponification with an excess of 0.1 N alcoholic sodium hydroxide under reflux. The method of Ogg, Porter, and Willits (11) was used for determination of free hydroxyl.

Specific rotations, listed in Table I, were determined in a 1-dm. tube. For these measurements, approximately 0.4 g. of ester was dissolved in 10 cc. of chloroform.

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